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ALLEGED NAPHTHA POISONING IN A RUBBER FACTORY,

With an Inquiry into the Effects of the Inhalation of Naphtha Vapor.

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A CASE OF ALLEGED NAPHTHA POISONING IN A RUBBER FACTORY, WITH AN INQUIRY INTO THE EFFECTS OF THE INHALATION OF NAPHTHA VAPOR.[1]

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MICHAEL KIRBY, about thirty years of age and weighing one hundred and sixty pounds, whose previous history is not well established, but who was considered healthy and not a drinker, while engaged in cleaning out a churn containing a mixture of rubber and naphtha was found dead in the churn at 2 P. M., although he was seen alive and apparently well about five or ten minutes before. He was removed from the churn and a doctor summoned, who pronounced it death from naphtha poisoning. No autopsy was held.

The churn, open at the top, was five feet one and one-half inches deep, and three and one-half feet in diameter, its capacity being about forty-eight cubic feet. In this receptacle was placed a mixture of rubber, whiting and very little sulphur with considerable naphtha, the whole being agitated by paddles which revolved in the churn. In the present case, the paddles for some reason stopped revolving, and it was decided to clean out the churn in order to learn the cause of the trouble. A trowel was found clogging the paddles, that Kirby had presumably let fall into the mixture. This was on September 4th, and Kirby was at once directed to clean the churn. As is customary in such cases, he drew off all that he could, namely, the more fluid portion, then got into the churn and baled out the rest.

[1] Read before the Boston Society for Medical Improvement, March 14, 1892.

No trouble was experienced from this. The work was resumed the two following days, and on September 7th he was told to finish it. There was then about three-quarters of an inch of the compound in the bottom of the churn, although it was nearly dried out, that is, there was little or no naphtha in it; and it was while he was at work on this, after his dinner, that he was found dead. It was not necessary for him to have his head nearer than arm's length from the bottom of the churn.

Very soon after this, two men got into the churn and remained about the same length of time that Kirby did after he was last seen alive, and they felt no ill effects from it. A week later, a man got in and finished cleaning it, and he, likewise, experienced no ill effects. Later, a man got into it when it was half full of "rubber stock," and worked there for half an hour. He did not notice the naphtha any more than he did when he was in the covering-room, where most of the men work.

The churn-room is 24¼ feet long, 15 feet 11 inches wide, and 12½ feet high, and contains 4,650 cubic feet. It has five large windows each 5 feet 5 inches wide and 7 feet 10½ inches high, two on the south side and three on the west. On the east is a door, 6 feet 9½ inches high and 2 feet 11½ inches wide, opening into a passage-way which leads to the outer air, the passage being 3 feet 10 inches wide and 13 feet 8 inches long. Huxley, in his "Elementary Physiology," page 100, says, "to be supplied with respiratory air in a fair state of purity, every man ought to have at least 800 cubic feet of space to himself, and that space ought to be freely accessible by direct or indirect channels to the atmosphere." The churn-room contained nearly six times the space needed for one man.

The churn was on the east side of the room on a

raised platform two feet three inches from the door-way. The top of the churn was five feet eleven inches below the ceiling and three inches below the top of the door-way, hence there was ample opportunity for circulation of air between the top of the churn and the ceiling, aided by the close proximity to the door-way.

At the time of Kirby's death, the door on the east side of the churn-room was wide open and also the outside door at the end of the passage; a south window was open six inches top and bottom, while another south window had a pane gone and one west window nearly opposite the door was down six inches from the top.

According to the weather report of that day, the wind averaged ten miles per hour from the north-east. The highest temperature was 77° F. in the afternoon. The humidity was high, 89 per cent. at 8 A. M., and 92 per cent. at 3 P. M. There was no rain.

In a room of the given size, with free access, by means of open doors and windows, to a wind blowing ten miles an hour, there could not have been any accumulation of vapor even if considerable naphtha had been exposed to evaporation. On the contrary, the evaporation of naphtha from the rubber stock in the churn at the time of the fatal accident must have been comparatively slow. First, because the amount of residual stock was small; secondly, because the residual stock could not have contained more than 20 to 30 per cent. of naphtha; and, thirdly, because the naphtha which remained in the stock was only slowly volatile.

The more fluid portion of the contents of the churn was drawn off on the afternoon of September 4th; on the 5th and 6th, more of the thick mixture was removed; and on the 7th, there was only a small layer of residual stock. During all this time evapo-

ration was going on; that is, the dangerous element in the mixture was gradually diminishing during the three days in which Kirby worked without detriment, until finally a residue was left from which evaporation of naphtha took place very slowly.

This is plainly indicated by the following experiment: 128 grammes of rubber stock from the bottom of a churn, after standing three days, were placed in a suitable retort, and the naphtha distilled and collected. It was heated by contact with boiling water for five hours, and as a result 25.5 grammes or 22.2 per cent. of naphtha distilled over; on raising the temperature still higher, to above 200° C., 12.9 grammes or 10 per cent. more naphtha was obtained, making a total of 32.2 per cent. of naphtha.

Naphtha is a volatile fluid, but when in contact with rubber and other material making up the rubber stock it is apparently held tenaciously by this material, and its evaporation rendered a long and slow operation. In the experiment quoted above only a small quantity of material was taken and the mixture was heated for hours in boiling water, under conditions by which free naphtha would have been quickly evaporated off, yet it required over six hours continuous heating, a portion of the time at a temperature more than three times above the boiling point of naphtha before all of the latter could be removed from the rubber mixture.

Further, the evaporation of the naphtha was throughout the entire experiment a gradual process; at no time did a rapid distillation occur. Other experiments leading to the same result are as follows:

Two specimens of rubber stock, of the same thickness and consistency as that in the churn at the time of Kirby's death, were placed in sealed jars, and one labelled "No. 1, February 16th," the other, "No. 2, February 17th"; 524 grammes of the mixture from No.

1 yielded, by long-continued distillation, 144 grammes of naphtha or 27.4 per cent., while 641 grammes from No. 2 gave only 133 grammes of naphtha or 20.7 per cent as a result of several hours' heating at a high temperature. These last two experiments confirm the preceding in showing that the naphtha held in the churn stock does not evaporate readily as free naphtha would, but is held tenaciously by the rubber mixture: further, the experiments show that there had evaporated 6.7 per cent. of naphtha as a result of one day's exposure of the rubber stock in the churn.

These results lead to the conclusion that on September 5th and 6th Kirby must have been exposed to a more dangerous atmosphere, or at least one more charged with naphtha, than on September 7th, when there was a much smaller amount of stock, and this contained a much smaller proportion of naphtha.

Let us now look at the nature of the naphtha in the churn. Naphtha is made up of a number of closely related hydrocarbons from the distillation of petroleum. These hydrocarbons are of low specific gravity, that is, are lighter than water and have a comparatively low boiling point, the naphtha representing the lighter and more volatile portions of petroleum, in distinction, for example, from kerosene and other higher boiling products. Commercially, naphtha and benzine are essentially the same, but naphtha, or as it is sometimes called, petroleum ether, is, strictly speaking, a lower boiling product and hence more volatile than benzine. But, as a matter of fact, the naphtha used so extensively for manufacturing purposes in this country is a mixture of naphtha No. 0, No. 1, No. 2 and benzine.

The naphtha used in the factory where Kirby was employed was examined, and it was found to have a specific gravity of 0.681, and contained about 37 per

cent. by volume of hydrocarbons with a boiling point below 70° C.; in other words, 37 per cent. of the naphtha was volatile at a temperature of 70° C. The great difference in volatility between that portion of the naphtha distilling below 70° C. and that portion boiling or distilling above 70° C. — a point of considerable significance in this case — is made strikingly manifest by the following experiment: Two equal portions of naphtha, one the fraction distilling below 70° C., and the other the fraction distilling above 70° C., were exposed to the air, side by side in uncovered dishes at the ordinary room temperature, for six hours. As a result, it was found in measuring the naphtha remaining in the two dishes, that of the portion distilling below 70° C., 25 per cent. had evaporated, while of the portion distilling above 70° C., only 8.5 per cent. had evaporated. Now, the more volatile portions of naphtha are obviously the most dangerous. In all cases where persons are exposed to naphtha vapors the lower boiling hydrocarbons would be the first to volatilize, and their action would naturally be the most pronounced, and under ordinary circumstances the larger the proportion of these more volatile products, the greater would be the danger from naphtha fumes. Dragendorff, Professor of Toxicology in Russia, says, "The higher boiling constituents of petroleum are hardly to be classed with poisons. There are cases where they have been borne in large quantities without harm."

A sample of rubber stock from the bottom of a churn, of the same consistency and character as that in the churn at the time of Kirby's death, yielded only two per cent. of naphtha boiling below 70° C. In other words, the exposure of naphtha in an open churn for two or three days, is followed by a fairly rapid evaporation of the more volatile hydrocarbons,

leaving a residue in which the heavier hydrocarbons predominate. Hence, it is obvious that the naphtha which remained in the residue of the churn stock Kirby was occupied in removing, must have been nearly or entirely free from those more volatile and dangerous portions of the naphtha which distil below 70° C.

Let us now consider the toxic action of naphtha as indicated by the result of experiments with animals. Over twenty distinct experiments were tried with rabbits and dogs, and where any toxic effect was produced the symptoms were essentially the same in every case. The animal was placed in a large can open at the top; on the bottom of the can was placed a quantity of naphtha, the animal sitting or standing on an inverted wire sieve, which raised him a few inches from the naphtha and kept him out of it, although allowing free passage of the vapors. At times, the top of the can was covered with wire netting to prevent the animal from jumping out. There was no rubber to retard the evaporation and the naphtha (76° Baumé) contained the full amount of the more volatile hydrocarbons.

Restlessness was the first symptom noticeable and in no experiment did the action of the naphtha at first extend to such a point that the animal could not jump out of the can if allowed to do so. In fact, the animal always attempted to leap out. On being restrained, it gradually became weaker and ceased to attempt escape, the teeth grinding together and then, sooner or later, there invariably came a point when the animal fell over and was attacked by violent convulsions, the body being curved or arched, the legs rigid, the facial muscles drawn back, exposing the teeth and jaws, the mouth stretched open and the legs often quivering with convulsive tremors. On being removed from the can after a minute or two, the animal always recovered

after a short time, say thirty minutes. In no case were these attacks followed by death; weakness remained apparent for a short time, but the animals soon hopped about as usual. There was apparently no true anæsthesia, no direct narcotic effect produced, no tendency to fall into a stupor and sink away into a quiet death, but always, at the end, there came the terrible convulsion of marked opisthotonic character, shrill cries and effects which point plainly to spinal action, or to irritant action on the motor centres in the brain.

In Kirby's case there was no evidence of a violent, convulsive death, no clinched fingers, staring eyes, distorted features, and he made no outcry. With rabbits, when the fumes of the naphtha have nearly taken possession of the animal, he instinctively raises his head above the top of the can and by breathing a little of the purer air above obtains a new lease of life.

Animals do not quickly succumb to the action of naphtha fumes, even when they are exposed to comparatively large quantities of free naphtha for some time. This point is well illustrated by the following experiment: A large dog, weighing twenty-eight pounds, was confined in a wooden box or cage lined with galvanized iron, two feet wide, three feet four inches long and two feet eight inches high; the bottom on which the dog stood was of heavy wire netting; under this was a tightly fitting iron tray, the bottom of which was five inches below the netting. The top of the tray was of wire netting and during the experiment was partially closed by towels laid over it.

The dog was placed in the cage at 9.30 A. M., and a little more than a quart of naphtha (76° Baumé) poured into the tray. The vapor rose through the cage, and the atmosphere in the room was charged with it. The animal remained there five hours without being noticeably affected.

In order to see how quickly death would result from naphtha under circumstances most favorable for its action, the same dog was held by two assistants, and a sponge and cotton saturated with the same naphtha were continuously held to his nose. Within five minutes he began to tremble, the pupils widely dilated, quickly followed by a violent convulsion, the limbs rigid, the facial muscles contracted, showing the teeth and jaws, blood oozed from the nose, frothy mucus or slime from the nose and mouth, and shrill cries. Fresh naphtha was continuously applied to the nose. Involuntary discharges of urine and fæces followed. The convulsions were so great that the two men could hardly hold him. It was a continual struggle, convulsion passing into convulsion, with occasional moments of comparative quiet with labored breathing. After twenty-five minutes, at the end of a violent convulsion, he sank down dead, without showing any tendency to sleep or stupor.

In order to note the different effects of the low and high boiling naphthas on animals, the following is instructive. Two rabbits of equal weight were taken. In the previously described can were placed 200 cubic centimetres of naphtha distilling below 70° C., that is, naphtha which was almost entirely wanting from the churn stock. The rabbit was placed on the sieve, and the top of the can covered by an inverted sieve. This was at 8.55. The rabbit became uneasy and restless at once. At 9.06 he was unsteady and swaying to and fro, head low down, jaws and teeth grating. At 9.07 he fell over in convulsions. At 9.08 he lay limp, breathing heavily. At 9.11, a slight convulsion, followed by a heavier one. At 9.12 he was taken out of the can and laid on the floor. At 9.14, recovering, but unable to use his legs, trembling on trying to walk. At 9.16, hopping about, apparently well.

In the same apparatus and under exactly the same conditions, the other rabbit was placed with 200 cubic centimetres of naphtha boiling above, instead of below, 70° C. This was at 9.27. At 10.15 he was unaffected. At 11.30, still all right, though apparently somewhat drowsy and weak. At 12.00, very quiet on the bottom of the sieve. Touched lightly he fell over, lay quietly for a moment, then fell over on his side without a convulsion. Finally, had a strong convulsion with shrill cries. Taken out and placed on the floor, he lay for some minutes scarcely breathing, then gradually recovered, though still weak in the legs. At 12.15 he was on his feet again, and hopping about as usual.

In this latter experiment, where the naphtha corresponds to that present in the residue of churn stock, we see that two and one-half hours elapsed before the animal was sensibly affected, while in the first experiment where the lower boiling naphtha was used the rabbit was in convulsions in twelve minutes. In both cases the mode of action was the same, the main difference being the rate of action. One other important point is brought out by the following: 200 cubic centimetres of naphtha distilling above 70° C. were poured into the can, a good-sized rabbit placed on the sieve, and an inverted sieve covered over the top of the can. This was at 9.55. At 10.58 the animal was quiet on the bottom of the can; at 11.18, ditto; at 12.00, fell over on his side; at 12.02, slight convulsion, then lay quietly on the bottom of the can, eyelids and facial muscles twitching; at 12.05, heavy convulsion.

In most of the experiments, the rabbits were removed from the can at this point and an opportunity given for their recovery. In this case, however, the animal was allowed to remain in the can. At 12.07, there were convulsive tremblings continuously, most pronounced in

the forelegs. The animal lay on its side, its head on the sieve, not more than three inches above the layer of naphtha, pupils contracted almost to a point. This condition continued till 12.35, when the convulsive tremblings were succeeded by a violent convulsion followed immediately by death, the head thrown well back, the mouth stretched wide open, and the lips drawn back. In the first part of this experiment we have simply a repetition of previous results; but after the heavy convulsion at 12.05, we see that death did not follow immediately, although the animal lay near the bottom of the cage with its head almost in the naphtha. Death was delayed half an hour, although the bottom of the can was covered with a layer of free naphtha.

In Kirby's case he was seen ten minutes before his death; the naphtha then in the churn must have been similar to that used in the last-mentioned experiment with the rabbit. We are obliged to conclude that, if these experiments illustrate the way that naphtha acts, then Kirby could not have been killed by naphtha.

Naphtha is used very extensively throughout New England, but we have been unable to learn of a single fatal case of naphtha-poisoning that has come to the notice of the medical examiners and chemists. At a large rubber factory in the vicinity of Boston, we were told that in the cloth-covering room, where a great many times as much naphtha is used as in the churn-room, there were formerly among the working-girls, many instances of "naphtha-drunk" or silliness, sometimes followed by unconsciousness. When the girl was taken into the air, she soon recovered and went to work again. It was principally hysterical girls and those who ate no breakfast who were thus affected. More ventilation in the room and obliging the girls to eat breakfast, put a stop to these unpleasant attacks.

In the *Revue des Sciences Médicales*, for 1888, Sury-Brienz publishes what he calls the first case of death from the vapor of benzine. A man, twenty-four years old, was working in a chemical factory. It was very cold out-of-doors. Against the rules, he went into a place where the toxic vapors were being formed, without opening doors and windows in advance. He fell dead immediately after coming out, but it is not stated how long he was there. The autopsy showed some softening of the brain, old adhesions of the lungs and some thickening of the cardiac valves from former disease. The other lesions, probably due to the benzine, were fluid blood, great lividity, congestions and some hæmorrhages. In this case, then, which is supposed to be the first fatal case in France, there is evidence of old disease of the brain, lungs and heart, and the benzine was inhaled in a fresh state, in a room where there was no ventilation.

Poincaré, a French authority, says there have been many cases of unconsciousness among workers in naphtha, but only one death. He gives no particulars of this one case, but it was before 1879. Lewin, a famous German writer on poisons, says that workers on rubber fabrics stand benzine without detriment to their health.

Felix, in the *Oeffentliches Gesundheitspflege*, for 1872, page 231, gives some experiments on healthy men. Into a paper cone, loosely filled with cotton wool, of which the point was cut off, pure benzine was poured, and held before the noses of several healthy men, as in giving chloroform. In the first eight minutes, the pulse rose and later fell. Five to fifteen grammes of benzine, inspired for from seven to twelve minutes produced dizziness, nausea, desire to vomit, cough, burning in the chest and sleepiness. Twenty to forty grammes inspired for eight to twenty

minutes produced sleep and full anæsthesia as by chloroform. The stupor lasted two to eight minutes, and after coming to, they complained of nausea, sleepiness, and headache. The very slow pulse returned to normal in ten to twenty minutes. Some persons bore the inspiration of fifty to fifty-five grammes without lasting disturbance.

Hirt, "Diseases of Occupation," 1875, Band 2, page 183, says he examined a great many workers in rubber, benzine and naphtha, and was astonished to find them exceptionally healthy. After a stay of several hours in benzine air, there was no trouble with pulse or respiration.

Poincaré, "Hygiène Industrielle," 1886, page 207, attributes the headache, pain, exhilaration followed by depression, to the bi-sulphide of carbon rather than to benzine. But bi-sulphide of carbon is very volatile, with a boiling point of 45° C., and cannot be present in the churn residue, which does not begin to boil until about 70° C.

In *L'Union Médicale*, Paris, 1861, page 92, is an article by M. Perrin. After some experiments on animals with benzine, he concludes that intoxication by benzine is very different from that by chloroform. In chloroform and ether, the ultimate and deadly period of intoxication does not exceed three or four minutes, while with benzine it may last five times as long without the death of the animal following. Benzine seems incapable of producing that complete and remarkable inanition and insensibility of the whole body which is a characteristic of the anæsthetic proper. The persistence of sensibility, which is only weakened, *the heavy convulsions* and the functional exaggeration of the circulation and the respiration, indicate that the nerve-centres are affected in a particular way, and that the physiological effects resemble closely those

which result from animals breathing the essential oils. a toxic dose of which causes drunkenness, convulsions and death without the animal passing through the state of true anæsthesia.

It would be possible to multiply experiments and quotations; but, in our opinion, we are justified in concluding that Kirby's death was not due to naphtha, because —

(1) He was accustomed to it.

(2) He had worked in the churn for several days without bad effect, when the naphtha was much more abundant, more volatile, more dangerous, than when he was found dead.

(3) The churn-room was well ventilated, and there was no possibility of accumulation of fumes.

(4) Experiments on animals, even with free, low-boiling naphtha, and continuously applied, show a mode of action and death entirely unlike the Kirby case.

(5) We are unable to find in medical literature any similar case to Kirby's, where it was known that death was due to naphtha.

(6) Cases of sudden death, particularly soon after dinner, in persons who were not known to have any cardiac or other serious disease, are sufficiently common to justify us in concluding that Kirby's death was due to some natural cause, and that it was not caused by naphtha.